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Medium perturbations on the molecular polarizability calculated within a localized dipole interaction model

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We have studied the medium effects on the frequency-dependent polarizability of water by separating the total polarizability of water clusters into polarizabilities of the individual water molecules. A classical frequency-dependent dipole–dipole interaction model based on classical electrostatics and an Unsöld dispersion formula has been used. It is shown that the model reproduces the polarizabilities of small water clusters calculated with time-dependent density functional theory. A comparison between supermolecular calculations and the localized interaction model illustrate the problems arising from using supermolecular calculations to predict the medium perturbations on the solute polarizability. It is also noted that the solute polarizability is more dependent on the local geometry of the cluster than on the size of the cluster. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1494418]

I. INTRODUCTION

Since the factors determining the linear and nonlinear optical (NLO) response properties of single molecules are becoming more clear and the existence of highly accurate methods to calculate these properties, the design of new NLO materials at the molecular level is becoming feasible.[1–4] However, in molecular crystals, molecules in solution and polymeric materials the properties of the individual molecules are perturbed by interactions with the surrounding medium. These intermolecular effects can have significant influence on the (hyper) polarizabilities of the molecules.[5–11]

The presence of a medium (solvent) will affect the molecule (solute) in two ways. First, the externally applied fields are modified and, second, there is an explicit solute–solvent interaction. The modulation of the applied fields is in general treated by means of local field factors, which will not be discussed here, but the reader is referred to, e.g., Refs. 12–14. The solute–solvent interactions are most commonly taken into account by adopting the so-called continuum model; see, e.g., Refs. 7, 8, 15, and 16. The greatest disadvantage of the continuum models is the neglect of the explicit microscopic structure of the solvent. In a supermolecular calculation the solvent molecules are taken into account explicitly and treated at the same level of theory as the solute. This type of brute force method allows only the nearest-neighbor molecules to be included. An alternative is a combination of the continuum model and supermolecular calculations, the so-called semicontinuum model.[7,17,18]

Although the supermolecular methods are accurate (within the chosen model) the properties obtained are for the total supermolecule or cluster. Unless the molecular property of interest is additive the problem of partitioning the total response into local contributions remains. This resembles the problem of extracting information about molecular properties from experimental macroscopic properties. Therefore, understanding the response properties of the bulk materials, the individually molecules and the perturbations caused by environmental interactions are needed in order to achieve an efficient procedure for designing optical molecular materials at the atomic level.[1–3,19]

Therefore we will in this paper discuss possible ways of partitioning the total polarizability into local contributions. Three general partitioning schemes for any supermolecular type of calculation will be discussed. Also, a classical localized model in which the medium effect on the molecular polarizability can be calculated is presented. The method is a modification of a classical dipole interaction model[20–23] for calculating the molecular polarizability. The results from the model will be compared with time-dependent density functional theory (DFT) calculations.

II. DISTRIBUTED POLARIZABILITIES OF INTERACTING MOLECULES

A. General partitioning schemes

In general a proper partitioning scheme should be additive,[24] i.e., the sum of effective properties of the individual molecules in the total aggregate. The simplest way of constructing the effective polarizabilities is treating all molecules as identical, i.e., to calculate the polarizability per molecule (PPM) α/N. Since the PPM model gives an average quantity it is useless for retrieving information about a specific member in the cluster such as a solute molecule in solution. A simple alternative to the PPM model is the ''differential shell'' approach (DSA).[7,25] In DSA the solute polarizability is defined as the difference between the polarizability of the cluster and the polarizability of the solvent. Information about a specific member of the cluster can be obtained at the expense of one extra calculation. Therefore,

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the model can also be used for systems where the solute molecule is different from the surrounding solvent molecules.

If we expand the total polarizability, α^{tot}, in a cluster sum[26,27] we can write the interaction polarizability as

$$\Delta\alpha^{\mathrm{tot}}=\alpha^{\mathrm{tot}}-\sum_i \alpha^i=\sum_{i<j}\Delta^{ij}\alpha^{(2)}+\sum_{i<j<k}\Delta^{ijk}\alpha^{(3)}+\cdots, \tag{1}$$

where α^i is the polarizability of the isolated monomers and $\Delta^{ij}\alpha^{(2)}$ is the induced polarizability arising from interaction between molecule i and j. Similarly $\Delta^{ijk}\alpha^{(3)}$ is the nonadditive three-body polarizability of molecules i, j, and k. Using the above-mentioned expansion of the interaction polarizability we can define a partitioning of the cluster polarizability into a many-body corrected polarizability, α^{MBP}, as

$$\alpha^{\mathrm{MBP}}=\alpha^p+\sum_j W_{pj}^{(2)}\Delta^{pj}\alpha^{(2)}+\sum_{j,k} W_{pjk}^{(3)}\Delta^{pjk}\alpha^{(3)}+\cdots, \tag{2}$$

where $W_{pj}^{(2)}$ and $W_{pjk}^{(3)}$ are appropriate weight factors chosen such that Eq. (1) is fulfilled. A simple choice of weights would be to divide the interaction polarizability equally among the molecules. Another, more general method but also more difficult, is a weighted assignment. The weighting could, e.g., be done with the vacuum polarizabilities of the isolated molecules as

$$W_{\alpha\beta}^{ij}=\frac{|\alpha_{\alpha\beta}^j|}{|\alpha_{\alpha\beta}^j|+|\alpha_{\alpha\beta}^i|}. \tag{3}$$

This weighting scheme is dependent on the different types of molecules involved and also on the orientation of the molecules. A major drawback of the MBP approach is that it requires many calculations in order to determine the interaction polarizabilities. However, for pure liquids, such as water, the two different weighting schemes will be nearly identical and the method can be used as a test of other partitioning schemes.

B. The localized dipole–dipole interaction model

An elaborate model, but yet very simple compared with quantum chemical calculations, is the dipole interaction model of Applequist *et al.*[20,28] based on the earlier work of Silberstein.[29–31] In the interaction model (IM), the atoms of a molecule in an external field interact by means of their atomic induced dipole moments according to classical electrostatics. Even if the atomic parameters are isotropic polarizabilities, an anisotropy of the molecular polarizability is introduced by interactions with the surrounding atoms.

Considering a set of N interacting atomic polarizabilities, the atomic induced dipole moment due to an external electric field, E^{ext}, is given by

$$\mu_{p,\alpha}^{\mathrm{ind}}=\alpha_{p,\alpha\beta}\left(E_\beta^{\mathrm{ext}}+\sum_{q\neq p}^{N} T_{pq,\beta\gamma}^{(2)}\mu_{q,\gamma}^{\mathrm{ind}}\right), \tag{4}$$

where $T_{pq,\alpha\beta}^{(2)}$ is the interaction tensor which has been modified according to Thole[21] to include a damping term

$$T_{pq,\alpha\beta}^{(2)}=\frac{3f_{pq}^T r_{pq,\alpha}r_{pq,\beta}}{r_{pq}^5}-\frac{f_{pq}^E\delta_{\alpha\beta}}{r_{pq}^3}. \tag{5}$$

The screening functions in Eq. (5) are given by[22]

$$\begin{aligned} f_{pq}^E&=1-[1+s_{pq}+\tfrac{1}{2}s_{pq}^2]\exp(-s_{pq}),\\ f_{pq}^T&=f_{pq}^E-\tfrac{1}{6}s_{pq}^3\exp(-s_{pq}), \end{aligned} \tag{6}$$

where the term s_{pq} is given by $s_{pq}=ar_{pq}/(\alpha_p\alpha_q)^{1/6}$, with a the screening length, and α_p the atomic polarizability of atom p.

The molecular polarizability can be written as[20]

$$\alpha_{\alpha\beta}^{\mathrm{mol}}=\sum_{p,q}^{N} B_{pq,\alpha\beta}, \tag{7}$$

where $\mathbf{B}$ is the relay matrix defined in supermatrix notation as

$$\mathbf{B}=(\boldsymbol{\alpha}^{-1}-\mathbf{T}^{(2)})^{-1}. \tag{8}$$

Well below the first electronic absorption, the frequency dependence of the molecular polarizability is often approximated with an Unsöld-type of expression.[3] Here we assume that the atomic polarizability has a similar frequency dependence[23]

$$\alpha_p(-\omega;\omega)=\alpha_p(0;0)\times\left[\frac{\overline{\omega_p^2}}{\overline{\omega_p^2}-\omega^2}\right], \tag{9}$$

where $\overline{\omega_p}$ is an atomic parameter describing the frequency dependence.

In order to calculate the polarizability of the solute molecule in the presence of the solvent molecules we utilize a localized interaction model (LIM). This is done first by decomposing the relay matrix into a block diagonal form with blocks, $\tilde{B}_{ii}$, corresponding to a relay tensor for the ith molecule or subgroup. In the decomposition of the relay matrix an assignment of the interaction blocks $B_{i\neq j}$ to the diagonal blocks B_{ii} is needed. This is arbitrary but can be done similarly to the weighing in the MBP approach. Therefore, we have for molecule i,

$$\alpha_{\alpha\beta}^i=\sum_{pq\in i}\left(B_{pq,\alpha\beta}^{ii}+\sum_{j\neq i} W_{\alpha\beta}^{ij}B_{pq,\alpha\beta}^{ij}\right), \tag{10}$$

where W^{ij} is a weight factor either equal to $\frac{1}{2}$ or given by Eq. (3). The scheme where $W^{ij}=\frac{1}{2}$ is denoted LIM-1 and the scheme where the weights are given by Eq. (3) is denoted LIM-2.

III. COMPUTATIONAL METHODS

The atomic parameters α_p and $\overline{\omega_p}$ are obtained by fitting to the frequency-dependent polarizability of a single water molecule. The screening length parameter $a=2.130$ was taken from Ref. 22. For the benzene molecule only the carbon parameter, α_{C}, was optimized, leaving the hydrogen parameter to that obtained from water. The polarizabilities were obtained by TD-DFT calculations which are described in more detail in the following. The optimized atomic parameters are, $\alpha_{\mathrm{O}}=8.3955$ a.u., $\alpha_{\mathrm{H}}=0.3118$ a.u., α_{C}

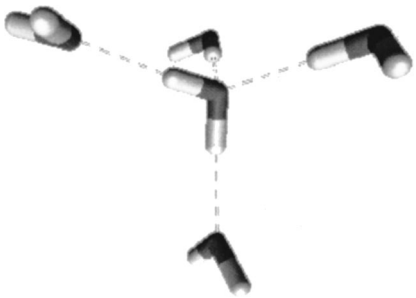

FIG. 1. A model of the structure of water molecules and the first solvation shell. The symmetry of the cluster is C_{2v}.

$=14.0775$ a.u., $\overline{\omega}_O=0.5426$ a.u., and $\overline{\omega}_H=\infty$. The frequency parameter for hydrogen indicates that all the frequency dependence in water is due to the oxygen atom.

For all the DFT calculations we used the RESPONSE code[32–34] in the Amsterdam Density Functional (ADF) program.[35–39] The ADF program uses basis sets of Slater functions. Here we used a triple zeta valence plus polarization and extra diffuse *s*, *p*, *d* functions (TZ2P+, in ADF basis set VI) were used. The van Leeuwen–Baerends (LB94) exchange-correlation potential[40] was used because of its correct asymptotic behavior.

The intramolecular geometry of the water molecules was that in gas phase, i.e., $R_{O-H}=0.958$ Å and $\angle_{HOH}=104.5°$. The solute water molecule was placed in the *xz* plane with the *z* axis bisecting the H–O–H angle. Experimental evidence[41,42] indicates that a tetrahedrally coordinated water molecule is present in liquid water and therefore we constructed a cluster containing the first solvation shell from Ref. 7. This tetrahedral structure has two donor hydrogen bonds and two acceptor hydrogen bonds (see Fig. 1). The O–O distance is $R_{O-O}=2.85$ Å. The geometry of the larger clusters ($N>5$) was obtained by molecular dynamics (MD) simulations keeping the first solvation shell fixed. The geometry of the benzene molecule was taken with standard bond lengths and angles from Ref. 43 and is placed in the *xy* plane with the *x* axis along a two-fold axis. The cluster containing benzene molecules was generated by MD simulations with one fixed solute in the center and 41 solvent molecules.

The MD simulations were performed with the DRF90 program[44] which uses a polarizable force field, consistent with the model used in this work. The MD simulation was done with the canonical *NVT* ensemble at a temperature of 298.15 K and a density of 0.9982 g/cm^3. The structure of the clusters was generated by first a 20 ps equilibration run followed by a 100 ps production run from which the lowest energy configuration was chosen.

IV. RESULTS AND DISCUSSION

In order to evaluate how well the dipole interaction model represents the polarizability of larger water clusters TD-DFT calculations were performed for the $N=5$ and $N=13$ clusters. These results are compared with the results obtained from the IM in Table I. We find in general good agreement between the TD-DFT results and the IM calculations. The largest deviations are for the $N=13$ cluster and are about 3% both in the static and frequency-dependent case. In particular, for the results of the first solvation shell ($N=4$) there is excellent agreement between the two methods. This indicates that the ''not so close'' interaction is particularly well described. At small distance basis set superposition errors (BSSE) start to influence the TD-DFT results and accounts for some of the deviations. Therefore, the results in Table I clearly illustrate that the dipole interaction model accounts for the static and frequency-dependent polarizability of these clusters and is therefore also capable of describing larger clusters.

The convergence of the MBP scheme was checked for the water pentamer. The calculations were done with the IM approach since it involves quite many calculations, i.e., five dimers, five trimers, three tetramers, and one pentamer. If TD-DFT were used, extensive corrections for BSSE would also have to be considered. It was found that the expansion converged by correcting for the three-body contributions. Also, the polarizability components changed by no more than 0.02 a.u. as the MBP expansion is taken beyond the pairwise terms. The tetramer contributions are an order of magnitude smaller than the trimer corrections and therefore it is to be expected in general that trimer contributions will be sufficient.

TABLE I. Frequency-dependent mean polarizability and polarizability tensor components of water clusters (in atomic units).

		$\omega=0.0000$ a.u.				$\omega=0.0656$ a.u.			
Method	N[a]	$\overline{\alpha}$	α_{xx}	α_{yy}	α_{zz}	$\overline{\alpha}$	α_{xx}	α_{yy}	α_{zz}
IM	1	9.15	9.83	8.40	9.21	9.28	9.97	8.53	9.34
TD-DFT	1	9.15	9.84	8.41	9.19	9.28	9.95	8.56	9.32
IM	4	36.65	34.78	39.36	35.81	37.17	35.28	39.91	36.32
TD-DFT	4	36.67	34.85	39.42	35.73	37.19	35.43	39.87	36.28
IM	5	46.40	45.39	48.24	45.57	47.06	46.05	48.92	46.22
TD-DFT	5	46.88	46.18	49.00	45.45	47.58	46.93	49.66	46.14
IM	13	116.56	115.27	117.98	116.43	118.15	116.85	119.56	118.04
TD-DFT	13	118.82	118.71	119.90	117.84	120.45	120.79	120.77	119.80

[a]Number of water molecules in cluster.

TABLE II. Comparison between LIM-1 and LIM-2 for calculating α^{solute}. All calculations were performed with the dipole interaction model and are given in atomic units. The clusters contains one solute molecule and forty-one solvent molecules.

	$\bar{\alpha}$	α_{xx}	α_{yy}	α_{zz}
		Water in water		
Vacuum	9.15	9.83	8.40	9.21
LIM-1	8.95	9.72	8.49	8.65
LIM-2	8.96	9.72	8.50	8.66
		Benzene in benzene		
Vacuum[a]	69.49	82.36	82.36	43.75
LIM-1	63.67	66.67	76.84	47.49
LIM-2	63.91	67.96	77.09	46.67
		Water in benzene		
Vacuum	9.15	9.83	8.40	9.21
LIM-1	8.62	10.56	7.63	7.66
LIM-2	7.99	10.88	6.88	6.21
		Benzene in water		
Vacuum[a]	69.49	82.36	82.36	43.75
LIM-1	69.94	82.36	80.01	47.44
LIM-2	72.78	86.39	85.61	46.34

[a]The TD-DFT results are: $\alpha_{xx}=\alpha_{yy}=82.36$ a.u. and $\alpha_{zz}=41.89$ a.u.

To determine the differences between the two partitioning schemes within LIM we also performed calculations on water in benzene, benzene in water, and benzene in benzene. The results are displayed in Table II. As expected, the results obtained with LIM-1 and LIM-2 are nearly identical for pure liquids. For the ''solutions'' the largest differences were found for water in benzene. If the polarizability of the solvent is much larger than that of the solute the weight factors in Eq. (3) become nearly unit and LIM-2 will give large differences compared with LIM-1. Therefore, the LIM-2 partitioning scheme should be used whenever the polarizability of the solute and solvent are different. However, in the rest of the work we only consider water and will therefore not distinguish between LIM-1 and LIM-2.

The results of comparing LIM with PPM, DSA and MBP are presented in Table III; they are all calculated with the IM approach. The MBP results for the water pentamer show an increase in all polarizability components compared with the vacuum results. There is a good agreement between LIM and MBP results indicating that LIM gives an accurate description of the ''solvation'' shift. The increase in the polarizability components predicted by DSA is about a factor of 2 larger than that predicted with MBP and for PPM the XX and ZZ components decrease while the increase in the YY component is almost five times larger than the MBP result. Therefore, we used the LIM model as a reference for comparing with results for the $N=13$ cluster for which the MBP approach becomes very tedious. For the $N=13$ cluster the LIM results predict a decrease in all polarizability components compared with the results obtained if only the first solvation shell is included. This trend is also found with DSA; however, the decrease in the polarizability components is much larger. Using PPM a decrease in all components is also found, but the polarizability is nearly isotropic in contrast to the results from both LIM and DSA. Therefore, in order to get an accurate description of the solvent shift in the polarizability tensor it is clearly necessary to go beyond simple models like PPM and DSA.

TABLE III. Comparison between LIM, PPM, DSA, and MBP for calculating α^{solute}. All calculations were performed with the dipole interaction model and are given in atomic units.

	$\bar{\alpha}$	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	α_{xx}	α_{yy}	α_{zz}
Vacuum	9.15	9.83	8.40	9.21				
		$N=5$[a]				$N=13$[a]		
LIM	9.55	10.33	8.74	9.58	9.21	9.91	8.17	9.56
PPM	9.28	9.08	9.65	9.11	8.97	8.87	9.08	8.96
DSA	9.75	10.61	8.88	9.76	8.98	9.60	7.73	9.60
MBP-3	9.46	10.24	8.66	9.49	⋯	⋯	⋯	⋯

[a]Number of water molecules in the cluster.

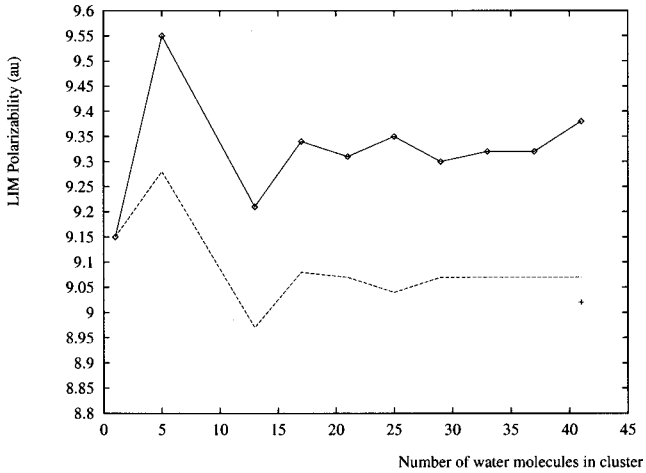

FIG. 2. Mean polarizability of a solute water molecule as a function of cluster size (in a.u.). All calculations were calculated with LIM-2 and PPM schemes. (—, ◇) LIM-2, (---) PPM and (+) indicates the LIM-2 result for the $N=41$ cluster with the structure of the first solvation shell relaxed.

In Fig. 2 we display the mean polarizability of a solute water molecule in water clusters as a function of the size of the cluster. The calculation has been performed with the LIM-2 method and the PPM scheme. To check the influence of the nearest-neighbor molecules we also performed a MD simulation where the structure of the first solvation shell was relaxed. The solute polarizability was again calculated with LIM and is also displayed in Fig. 2, which clearly illustrates that the solute polarizability is dependent on the size of the cluster. Both for LIM and PPM, large fluctuations are found for the smaller clusters, whereas the results are reasonably converged at a cluster size around $N=21$. The result for the cluster with the relaxed first solvation shell shows a large decrease of the mean polarizability. This indicates that the solute polarizability is more dependent on the local geometry of the cluster than on the actual size. Therefore it might be more important to include a larger number of different clusters than increasing the size of the individual clusters.

In order to get a better description of the local solvent structure we performed a MD simulation of 100 ps from which 100 randomly chosen configurations were picked. We used as starting configuration the $N=41$ cluster with the fixed first solvation shell. The solute polarizability was then calculated as an average over the 100 configurations. The

TABLE IV. Polarizability and solvation shift of a water molecule averaged over 100 randomly chosen solvent configurations with $N=41$. Calculated with the LIM-2 method. The results are in atomic units.

ω		$\bar{\alpha}$	α_{xx}	α_{yy}	α_{zz}
0.0000	Vac	9.15	9.83	8.40	9.21
	Solv	9.02±0.08	9.47±0.29	8.53±0.36	9.05±0.37
	Δ^a	−1.4	−3.7	1.5	−1.8
0.0656	Vac	9.28	9.97	8.53	9.34
	Solv	9.14±0.07	9.59±0.30	8.63±0.35	9.17±0.38
	Δ^a	−1.5	−3.8	1.2	−1.8

[a]Solvent shift as percentage.

results are displayed in Table IV, both for the static and the frequency-dependent polarizability at frequency $\omega=0.0656$ a.u. The mean polarizability of water is lowered by around 1.5% in going from vacuum to the cluster both in the static and in the frequency-dependent case. The largest changes, around 4%, were found in the X direction. This was also found for the static mean polarizability in an *ab initio* approach at the second-order Møller–Plesset (MP2) level where molecular interaction was accounted for by Coulombic interactions, although a lowering of around 4.6% was found.[10] The main difference in the two results can be explained from the difference in the vacuum polarizabilities predicted by, respectively, MP2 and TD-DFT.

V. CONCLUSION

In this work we have discussed the problems arising from using supermolecular calculations to predict the medium effect on a solute polarizability. Three different schemes for partitioning the polarizability of a cluster into local contribution are discussed. Within the dipole interaction model a partitioning scheme has been suggested which allows solvation effects on the molecular polarizability to be studied with a computationally cheap method. Results from small water clusters have been used to compare the different partitioning schemes which clearly illustrate the problems with supermolecular calculations. Also, the effect of different weighting schemes were examined using clusters where the solute molecule was different from the solvent molecules. The results from large water clusters indicate that the polarizability is more dependent on the local geometry of the solvent than on the actual size of the cluster. However, it is important to include more than the first solvation shell in the calculations.

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